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Journal of Molecular Structure (Theochem) 498 (2000) 233–246

THEO CHEM

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# Calculation of the structure and nuclear magnetic shielding constants of some H-bonded carbon acid complexes

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Received 30 April 1999; received in revised form 14 July 1999; accepted 6 August 1999

**Abstract**

Electronic and spatial structure of some H-bonded complexes ($(HCOOH)_n$ ($n = 1$–4), formic, acrylic acids and their complexes with water and dimethylsulfoxide) were studied by ab initio methods using MP2/RHF//6-31G*, RHF/6-31G* basis sets, and also by using density functional theory (DFT) within the B3LYP approximation. The possibility of formation of chain and cyclic complexes of formic and acrylic acids with dimethylsulfoxide is shown. In a cyclic complex two hydrogen bonds are formed. One is as usually with the O–H bond (S=O···H–O), the other is between the acid carbonyl group and one hydrogen atom of DMSO methyl groups (C–H···O=C). The calculations of nuclear magnetic shielding were carried out within a framework of the coupled Hartree–Fock method using gauge invariant atomic orbitals. Analysis of the results for various basis sets and comparison of the calculated and experimentally obtained chemical shifts show that the calculations predict a significant downfield shift for $^{1}H$ and $^{13}C$ nuclei for H-bonded systems. The results of calculations of $^{17}O$ magnetic shielding constants strongly depend on the used basis set and theoretical approach. 

*Keywords:* Nuclear magnetic shielding constants; Intermolecular interactions; Formic acid; Acrylic acid clusters; Complexes with DMSO and water; Ab initio calculations; B3LYP; MP2/RHF//6-31G*

## 1. Introduction

The study of the nature of intermolecular interactions and their influence on different types of the substance properties in condensed state is one of the timely problems in physical organic chemistry. A great number of publications, including monographs [1–5], and reviews [6] was devoted to the study of the intermolecular hydrogen bond mechanism and different aspects of its manifestation. Recently an interest in weak hydrogen bonding emerged in different fields of structural chemistry [7–9] and biology [10]. Highly urgent directions in literature are the study of hydrogen bond dynamics [11,12] and the influence of intermolecular interactions on the chemical reactions and, in particular, on transition states of the reactions [13–17].

Quantum chemical calculations of the electronic and spatial structure of various Van der Waals complexes of carbon acids and nuclear magnetic shielding constants of all nuclei in these systems have been carried out in the present work. Intermolecular interactions are extensively studied by different experimental methods, in particular, by NMR spectroscopy, which is well known for high-informative data it provides. Chemical shifts in NMR depend strongly on inter- and intramolecular interactions. Interpretation of experimental chemical shifts is highly difficult and sometimes is not unambiguous at the qualitative

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0166-1280/00/$ - see front matter 
PII: S0166-1280(99)00312-7